

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 000 097 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
25.09.2002 Bulletin 2002/39

(51) Int Cl.7: **C08F 10/00, B01J 8/24,
B01J 8/18, G05D 23/22**

(21) Application number: **98938100.9**

(86) International application number:
PCT/US98/15748

(22) Date of filing: **30.07.1998**

(87) International publication number:
WO 99/006451 (11.02.1999 Gazette 1999/06)

(54) CONTROL OF GAS PHASE POLYMERIZATION REACTIONS

KONTROLLE DER POLYMERISATIONSREAKTIONEN IN DER GASPHASE

CONTROLE DE REACTIONS DE POLYMERISATION EN PHASE GAZEUSE

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

(30) Priority: **31.07.1997 US 904164**

(43) Date of publication of application:
17.05.2000 Bulletin 2000/20

(73) Proprietor: **UNION CARBIDE CHEMICALS &
PLASTICS TECHNOLOGY CORPORATION**
Danbury, Connecticut 06817-0001 (US)

(72) Inventors:
• **KOCIAN, Harvey, Gene**
Victoria, TX 77904 (US)

• **REBHAN, David, Merrill**
Alum Creek, WV 25003 (US)
• **PARRISH, John, Roberts**
Cross Lanes, WV 25313 (US)
• **PILGRAM, Thomas, Walter**
Port Lavaca, TX 77979 (US)

(74) Representative: **Hayes, Adrian Chetwynd et al**
Boulton Wade Tennant,
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(56) References cited:
EP-A- 0 351 068 WO-A-94/28032
US-A- 4 249 907 US-A- 4 330 645
US-A- 5 352 749

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 000 097 B1

Descripti n**Backgr und of the Invention**

5 [0001] For exothermic reactions (e.g., polyethylene (PE) and polypropylene (PP) polymerization) in fluidized bed reactors many benefits are gained by maximizing cooling on both macroscopic and microscopic levels. Macroscopic in this case implies the total volume of the reactor whereas microscopic refers to the immediate vicinity around the catalytic sites where polymerization is taking place. When cooling improves, catalyst productivity and polymer properties often improve. At the same time, reactor operability becomes more robust since hot spotting, sheeting, and chunking are reduced.

10 [0002] One way of maximizing cooling throughout the reaction zone, and particularly on the microscopic level is by evaporative cooling. To this end, polymerization processes in which a certain portion of the cycle gas stream is condensed and fed to the reactor as a liquid where it vaporizes have been used (i.e., "condensing mode").

15 [0003] Condensing mode processes have been limited due to several factors including only an estimate of the amount of liquid entering the bed was controlled/monitored. Thus, depending on other process parameters, the instantaneous rate of liquid evaporation in the reaction zone was variable and was not controlled. The inability to independently control rate of liquid evaporation can cause oscillation/variation in reaction control variables like reactor pressure, temperature, bed weight, and fluidized bulk density. This in turn can cause variations in product properties and catalyst productivity. Additionally, the amount of liquid entering the bed has been estimated using the assumption of thermodynamic equilibrium. Thus, prior art methods have not been able to account for the dynamic nature of fluidized bed reaction system.

Summary of the Invention

25 [0004] The present invention provides a process for controlling a continuous gas phase exothermic process in a reactor having

- (1) a reactor inlet;
- (2) a reactor bed;
- (3) a reactor outlet; and
- 30 (4) a recycle line with (a) a compressor and (b) a heat exchanger;

with a pre-selected temperature for the reactor bed or outlet (2 or 3) and with a temperature differential (ΔT) between the temperature of the reactor inlet (1) and the pre-selected temperature of the reactor bed or outlet (2 or 3), comprising:

35 (A) controlling the heat transfer provided by the heat exchanger (4(b)) to maintain the pre-selected reactor bed (2) or outlet (3) temperature, while simultaneously

(B) controlling the feed rate to the reactor of a condensable fluid to maintain the temperature differential (ΔT) constant.

40 [0005] As outlined, the present invention encompasses a process for controlling a continuous exothermic gas phase process (e.g., polymerization) in a reactor having a reactor inlet, a reactor bed, a reactor outlet and a recycle line with a compressor and a heat exchanger with a selected temperature for the reactor bed or outlet and with a temperature differential between the reactor inlet and the reactor bed or outlet, wherein the reactor is operating in condensing mode by selecting a differential temperature (ΔT) set point consistent with the level of liquid hold up and rate of evaporation desired, where $\Delta T = T_e - T_i$ or $T_b - T_i$ given T_i and T_b , T_e and T_i are the reactor bed, reactor exit and reactor inlet temperatures, respectively. Thus, T_i is set by the desired ΔT . Given this set of conditions, the heat transfer provided by the heat exchange should be controlled to maintain T_b or T_e while simultaneously controlling the feed flow rate to the reaction of a condensable fluid to maintain ΔT .

Brief Description of the Drawing

55 [0006] Figure 1 is a schematic diagram of a polymerization process according to the present invention.

Detailed Description of the InventionReaction Process

5 [0007] The present invention is not limited to any specific type of continuous gas phase exothermic reaction and can be carried out in a stirred or fluidized bed reactor, except that it should be conducted using condensing mode, including the so-called "induced condensed mode", and "liquid monomer" methods. For example, fluidized bed process for producing polymer resins are practiced by passing a gaseous stream containing one or more monomers continuously through a fluidized bed reactor under reactive conditions in the presence of a polymerization catalyst. Product is withdrawn from the reactor. A gaseous stream of unreacted monomer is withdrawn from the reactor continuously and recycled into the reactor along with make-up monomer added to the recycle stream. Condensed mode polymerizations are disclosed in U.S. Patent Nos. 4,543,399; 4,588,790; 5,352,749; and 5,462,999.

10 [0008] In condensing mode processes this recycle stream, or a portion thereof, is cooled to a temperature below the dew point, resulting in condensing all or a portion of the recycle stream. The recycle stream is returned to the reactor. The dew point of the recycle stream can be increased by increasing the operating pressure of the reaction/recycle system and/or increasing the percentage of condensable fluids and decreasing the percentage of non-condensable gases in the recycle stream. The condensable fluid(s) may be inert to the catalyst, reactants and the polymer product produced; or it may be the monomers and comonomers used in the polymerization. The condensable fluid can be introduced into the reaction/recycle system at any point in the system. Condensable fluids include saturated or unsaturated hydrocarbons. Examples of suitable condensable fluids may be selected from liquid saturated hydrocarbons containing 2 to 8 carbon atoms (e.g., propane, n-butane, isobutane, n-pentane, isopentane, neopentane, n-hexane, isohexane, and other saturated C₆ hydrocarbons, n-heptane, n-octane and other saturated C₇ and C₈ hydrocarbons, and mixtures thereof); and polymerizable condensable comonomers (e.g., olefins, alpha-olefins, diolefins, diolefins containing at least one alpha olefin, such as propylene, 1-butene, isobutene, hexene, hexadiene, isoprene, styrene, octadiene, ethylidene norbornene, butadiene and mixtures thereof) may be used.

20 [0009] Liquid monomer polymerization mode may be employed, as is disclosed in U.S. Patent No. 5,453,471, U.S. Patent No. 5,834,571, PCT Application Nos. WO 96/04322 and WO 96/04323. When operating in the liquid monomer mode, liquid can be present throughout the entire polymer bed provided that the liquid monomer present in the bed is adsorbed on or absorbed in solid particulate matter present in the bed, such as polymer being produced or fluidization aids (e.g., carbon black) present in the bed. The liquid monomer process comprises continuously introducing a stream of one or more monomers and optionally one or more inert gases or liquids into the polymerization zone; continuously or intermittently introducing a polymerization catalyst into the polymerization zone; continuously or intermittently withdrawing polymer product from the polymerization zone; and continuously withdrawing unreacted gases from the zone; compressing and cooling the gases while maintaining the temperature within the zone below the dew point of at least one monomer present in the zone. If there is only one monomer present in the gas-liquid stream, preferably there also is present at least one inert gas.

Control Method

40 [0010] The control method of the present invention maintains a steady rate of liquid evaporation in the reaction zone while maintaining only a gas phase in the recycle line prior to the compression or cooling of the recycle gas. The difference between the reactor exit (T_e) or bed (T_b) temperature and reactor inlet (T_i) temperature, ΔT , which is related to the amount of liquid evaporation occurring on a steady state basis in the reaction zone, can be used to control the liquid evaporation. This can be achieved because the evaporation process takes place at a relatively constant temperature.

45 [0011] For the case of no evaporation (no liquid inventory), ΔT is at a maximum for a given production rate since the heat generated by reaction is transferred to the recycle gas stream as sensible heat. As liquid inventory increases, a portion of the heat generated by reaction is used for the evaporation process. Thus, as the amount of liquid evaporation increases (and the amount of liquid entering the bed increases), ΔT becomes smaller. By controlling ΔT , one can control evenly the rate of liquid evaporation in the reaction zone (i.e., the instantaneous liquid inventory in the reaction zone). Thus, sensitive control of the amount of liquid evaporation occurring in the reaction zone can be accomplished based solely upon two temperature measurements.

50 [0012] With the present control method the reactor temperature gradient becomes more stable on a macroscopic level and more uniform on a microscopic level. Hot spots, wall effects, and catalyst site overheating are minimized. Additionally, pressure, temperature, and gas chromatograph analysis do not swing due to uncontrolled evaporation/condensation of cycle gas. The reactor bed weight and fluidized bulk density do not swing due to changing levels of liquid inventory in the bed. Product consistency and reproducibility improves due to more stable control of operating parameters. The production rate is stabilized due to the stabilization of the variables listed above, which in turn allows

for increasing of average reactor rates. Generally, catalyst productivity will increase as liquid inventory increases, which will reduce catalyst costs and product ash content.

[0013] The present method is different from other control methods in that the extent of vaporization in the reaction zone is inferred by production rate and a temperature difference, rather than a less reliable and more complex estimate of condensation at the reactor inlet. This provides a "direct measure" of evaporative cooling in the reaction zone.

[0014] T_i may be measured at the bottom of the reactor or along the recycle line, after the heat exchanger and compressor and preferably after the feed line(s). If the T_i is measured in the recycle line before the feed line(s), then adjustment should be made to compensate for any heating or cooling of the recycle stream by the feed material. T_b may be measured in the reactor above the fluidization zone of the reactor bed, at the reactor outlet or in the recycle line before the compressor and/or heat exchanger. T_b may be measured in the fluidized bed, preferably in the top half of the bed. It is preferred to make the measurement above the maximum height of liquid penetration.

[0015] Selecting reactor pressure and composition to ensure condensing mode depends on the reactor design and the particular reaction, as well as desired production rate and product requirements. Such selections and determinations are well within the abilities of one of ordinary skill in the art. Certain considerations in such selection will be clear from the other requirements of this system set forth below.

[0016] In one embodiment of the present invention with reference to Figure 1, there is a reactor 1, with a reaction zone 2 and disentrainment zone 2a, a recycle line 3, which has a vent line 3a, and which passes through a compressor 4 and a heat exchanger 5 before reentering the reactor. Though re-entry is shown at the bottom of the reactor, such re-entry may be at other locations in the reactor and may be split into several feed lines. There is a condensable fluid agent feed line to the recycle line 6 with control valve 7. There is a coolant control valve 8 for the heat exchanger 5. There are three thermocouples 9, 10, 11 which measure T_e , T_b , and T_i , respectively. Bed temperature and differential temperature ΔT are maintained simultaneously via controller 12. There are inputs for bed temperature set point 12a and ΔT set point 12b, as well as a temperature measurement switch 12c which can be switched between measuring T_e and T_b . Controller 12 manipulates valve 8 to control T_b or T_e and also valve 7 to control ΔT .

[0017] Product may be withdrawn from the reactor (2, 2a) while reactants may be fed with the condensable fluid, or separately into the reactor or recycle line.

[0018] The measured ΔT is related to reactor control parameters for steady state operation as follows:

$$\Delta T = \frac{(P.R.)(\Delta H_r) - (\dot{m})(x_l)(\Delta H_v)}{(\dot{m})(1-x_l)(C_p)_{cyclegas}}$$

where (P.R.) = production rate, (ΔH_r) = heat of reaction, (\dot{m}) = cycle gas stream mass flow rate, (x_l) = mass fraction of liquid in the cycle gas stream at reactor inlet, (ΔH_v) = heat of vaporization, and $(C_p)_{cyclegas}$ = heat capacity of the cycle gas.

[0019] ΔH_r , $C_{p_{cyclegas}}$ and ΔH_v are constants; P.R. is set by catalyst and reactant flow rates; \dot{m} is a function of pressure, cycle gas composition, and compressor operation; and x_l is a function of the liquid monomer feed rate and liquid from the heat exchanger. Thus, several parameters must be controlled to maintain a constant ΔT .

[0020] The preferred way to control ΔT is to vary the condensable fluid agent feed rate or composition while maintaining the other variables constant. This is preferred because:

- 1) P.R. usually is determined by commercial necessity and so typically only is varied as needed to maximize production rates.
- 2) Cycle gas flow rate (\dot{m}) may be varied to affect control; but generally is not acceptable for fine control, as cycle gas flow rate affects other critical variables such as fluidization quality.
- 3) The heat exchanger typically is operated to control constant T_b or T_e , not ΔT . Also, liquid condensation in the heat exchanger is a function of several reaction parameters and is not controllable independently.

[0021] The present process has certain stability and operational limits, which are both steady state and dynamic. Three specific limits are

- 1) The total heat generated by reaction must be greater than or equal to the total heat required for liquid vaporization.

For steady state operation,

$$(P.R.)(\Delta H_r) \geq (\dot{m})(x_l)(\Delta H_v);$$

and in dynamic operation,

$$\int_0^t [(P.R.) (\Delta H_r)] dt \geq \int_0^t [\dot{m}(x_l) (\Delta H_v)] dt$$

5

where t is a characteristic time scale of the reaction system. This limit stipulates that stable, steady operation only can be maintained when the total heat generated by reaction is sufficient to vaporize all the liquid entering the reaction zone for a characteristic time. If the heat generated by reaction is less than the heat required to evaporate the incoming liquid, then liquid inventory will increase and flooding may occur, resulting in poor fluidization, mixing, or similar problems. Hence, this limit defines the upper limit for inlet liquid flow during steady state operation. When the heat generated by reaction equals the heat required for liquid vaporization, then ΔT is at its minimum. For a single component $\Delta T = 0$ at this condition. For multicomponent mixtures ΔT can be different from zero due to changing composition of the liquid and vapor phases during the evaporation process.

10

15

2) ΔT must be less than or equal to the temperature difference which would exist for no liquid evaporation (i.e., all sensible heat), i.e.,

$$\Delta T \leq \frac{(P.R.) (\Delta H_r)}{(\dot{m})(C_p)_{\text{cycle gas}}}$$

20

Note that this equation assumes there is no liquid in the cycle gas stream prior to the compressor and the heat capacity of the cycle gas is calculated at reaction temperature and pressure. The upper control limit for ΔT is defined when it equals the value defined by the above ratio.

25

3) The process needs to display a degree of predictable behaviour for appropriate application of the invention. Specifically, an increase in the liquid fraction of the entering stream should result in either constant or increased production rate, with other independent variables (catalyst feed, reactor temperature, etc.) held constant. This condition can be expressed mathematically as follows.

30

$$\left. \frac{\partial (P.R.)}{\partial [\dot{m}(x_l)]} \right|_{\substack{\text{Catalyst Feed,} \\ \text{Other Independent} \\ \text{Variables Constant}}} \geq 0$$

35

40

This requirement is related to the process itself. The operating restriction involved requires that an increase in the liquid fraction entering the reactor does not itself cause reduction in production rate at steady state. Variations in catalyst productivity or feed rate do not necessarily limit applicability of the invention, unless such variables are correlated with the liquid fraction variations at steady state.

45

[0022] The temperature of the reactor inlet stream (T_i) can be operated in a range slightly larger than that defined by the bubble point and dew point temperatures of the cycle gas stream. This ensures that liquid is entrained into the reaction zone and also accounts for some deviation from thermodynamic equilibrium (i.e., dynamic behavior). Liquid is formed both by condensation in the cycle gas heat exchangers and by make-up of fresh condensable fluid through the feed line 6. The minimum ΔT is defined by 'operating limit #1' above. This gives the maximum (x_l) for the pressure/composition of the cycle gas stream at the reactor inlet. The maximum ΔT for control is defined by 'operating limit #2' above, $x_l = 0$. Operation with ΔT 's between this range will result in a range of liquid evaporation rates with 0-100% of the heat of reaction being removed by liquid evaporation.

50

[0023] Optimum ΔT 's for control purposes are a function of many variables including superficial gas velocity, total cycle gas flow, cycle gas density, cycle gas heat capacity, cycle gas heat exchanger size and efficiency, cycle gas composition, and fluidization parameters such as resin morphology, fluidized bed density bed weight, solubility of liquid phase in polymer, etc. Since, in most instances, it is desired to maintain a constant average T_b , the composition, T_i , and pressure of the cycle gas inlet stream may be chosen to give a desired (x_l) for a given average reactor T_b .

55

[0024] The amount of liquid entering the reaction zone is determined by the rate of condensation in the heat ex-

changer and the amount of liquid added as fresh feed. For example, in the manufacture of polypropylene, ΔT is controlled by make-up of fresh liquid propylene such that propylene feed is increased to reduce ΔT or decreased to increase ΔT . For polyethylene production, a similar strategy can be used whereby the flow of a condensing agent, e.g., hexane, is varied to maintain a constant ΔT . For systems which use an inert condensable fluid, a vent stream must also be

available to remove the inert condensable fluid when needed (e.g., production rate slow-down, idling, shutdown, etc.) [0025] The temperature in the lower region of the reactor bed where some liquid is present essentially remains at T_i . In the upper region of the reactor bed, where no condensate is present, a temperature gradient exists which increases in the direction of cycle gas flow. Thus, when the ΔT across the reactor is decreased, liquid penetration into the resin bed is increased.

[0026] Depending on the concentration and physical properties of the condensing agent used, various dew point temperatures can be achieved which best suit polymer production. For polypropylene production, propylene can be used. For polyethylene production numerous inert hydrocarbons can be used, including propane, butane, isopentane, pentane, hexane, etc. By changing the concentration and/or composition of the inert hydrocarbon(s), cycle gas stream compositions can be specified which result in condensing mode operation over a wide range of specified average bed temperatures. Thus, the control of reaction zone liquid evaporation rate can be extended over a broad range of desired operating temperatures. These principles can be used to stably control reaction zone liquid evaporation for any exothermic fluidized bed reaction.

[0027] The ΔT and T_b or T_c control function (12) can be accomplished using a variety of methods. The controller manipulates the influx of feed, especially the condensable fluid, to control the ΔT , while also controlling the coolant flow in the heat exchange systems to maintain T_b and T_c . Algorithms for such control are known to those of skill in the art and the specific heat and/or mass balances depend on the particular system. In open-loop stable systems, model based methods such as Dynamic Matrix Control or Internal Model Control techniques can be readily applied by those skilled in the art. In open loop unstable systems, control can be accomplished using analog-type (e.g., PID) functions or other more sophisticated model based techniques. In a polyethylene application, the control function manipulates the cycle gas heat exchanger cooling water system and a condensable fluid feed. In a polypropylene system, the function manipulates the cycle gas heat exchanger cooling water system and the condensable reactant feed (i.e., propylene). Many other alternatives for accomplishing the ΔT and T_b or T_c control are usable, as long as the principles of operation (1-3) are maintained.

Polymers

[0028] Illustrative of the polymers which can be produced in accordance with the invention are the following: ethylene homopolymers and ethylene copolymers employing one or more C_3 - C_{12} alpha olefins; propylene homopolymers and propylene copolymers employing one or more C_4 - C_{12} alpha olefins; two reactor polymers, including impact polypropylene copolymers; polyisoprene; polystyrene; polybutadiene; polymers of butadiene copolymerized with styrene; polymers of butadiene copolymerized with acrylonitrile; polymers of isobutylene copolymerized with isoprene; ethylene propylene rubbers and ethylene propylene diene rubbers; polychloroprene, and the like.

Catalysts

[0029] Catalysts as are known in the art may be used, including, but not limited to, Ziegler-Natta, single site, and metallocene types, as disclosed in U.S. Patent Nos. 4,393,182, 5,106,806, 5,455,366, 5,329,033, 5,145,819, 5,317,036, 5,693,727 and PCT Application No. WO96/23010.

Example 1: Polyethylene Production

[0030] Thermodynamic models were used to simulate the relative amounts of liquid and gas phases and thermodynamic properties of the phases as a function of temperature, given a constant overall composition and pressure and assuming equilibrium. Then, a set of reaction conditions were picked to simulate real plant operation. Using the data, the " ΔT across the reaction zone" and "% Reaction Heat Removed by Vaporization" were calculated. Also, the limits of the method were calculated, ΔT with no liquid evaporation and the wt. % liquid corresponding to 100% reaction heat removed by evaporation ($\Delta T=0$ was assumed for this case to simplify the calculation.). The example shows how ΔT across the reaction zone can be used to control liquid evaporation in the reaction zone.

Overall Pressure: 2.07 MPa (295 psi)

Overall Reactor Composition (mol %): C_2H_4 = 0.333, isopentane = 0.093, C_6H_{12} = 0.047, C_6H_{14} = 0.009, H_2 = 0.06, N_2 = 0.458.

Calculated Dew Point = 75.7°C

EP 1 000 097 B1

Heat of Polymerization 3721600 J/kg (1600 BTU/lb)

Production Rate = 7131 g/s (56,600 lb/hr)

Cycle Stream Mass Flow Rate = 303655 g/s (2,410,000 lb/hr)

Average Gas Heat Capacity over 30-80°C \cong 1814 J/kg-°C (0.78 BTU/lb-°C)

5 Average Liquid Heat of Vaporization over 30-80°C \cong 188173 J/kg (80.9 BTU/lb)

ΔT_{max} Across Reaction Zone (i.e., no evaporation) \cong 48.2°C

Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % Reaction Heat Removed by Vaporization) = 46.4

10

15

20

25

30

35

40

45

50

55

Inlet Temp (°C)	30	40	50	55	60	65	70	75	80	85
Wt. % Liquid	27.1	23.2	18.3	15.5	12.3	8.8	5.0	0.7	0.0	0.0
Enthalpy of Gas (kJ/kg-mol) ((BTU/lb-mol))	9085 (3906)	9651 (4149)	10213 (4391)	10497 (4513)	10779 (4634)	11062 (4756)	11344 (4877)	11630 (5000)	11914 (5122)	12200 (5245)
Enthalpy of Liquid (kJ/kg-mol) ((BTU/lb-mol))	-7611 (-3272)	-5815 (-2500)	-4015 (-1726)	-3112 (-1338)	-2207 (-949)	-1298 (-558)	-384 (-165)	537 (231)	1531 (658)	2542 (1093)
Gas Heat Capacity (kJ/kg-°C) ((BTU/lb-°C))	2.0 (0.86)	1.93 (0.83)	1.88 (0.81)	1.84 (0.79)	1.81 (0.78)	1.74 (0.75)	1.74 (0.75)	1.70 (0.73)	1.70 (0.73)	
Liquid Heat of Evaporation (kJ/kg) ((BTU/lb))	240.3 (103.3)	219.1 (94.2)	199.1 (85.6)	189.1 (81.3)	178.9 (76.9)	169.1 (72.7)	158.6 (68.5)	149.8 (64.4)		
Ave. MW of Gas	28.3	29.2	30.1	30.7	31.4	32.1	32.8	33.6	33.7	33.7
Ave. MW of Liquid	69.5	70.6	71.5	72	72.6	73.1	73.6	74.1		
ΔT across reaction zone (°C)	27.5	31.4	35.7	38	40.4	42.8	45.3	47.8	48.2	48.2
% Reaction Heat Removed by Evaporation	58.3	49.9	39.4	33.4	26.5	18.9	10.8	1.5	0.0	0.0

Example 2: Polyethylene Production; Effect of Composition

[0031] Example 2 is similar to example 1, but details the effect of changing isopentane and nitrogen mol fraction at constant temperature. The simulation shows how liquid addition and deletion to the cycle flow can be used to control ΔT across the reaction zone (i.e., % Reaction Heat Removed by Vaporization) at constant reactor inlet temperature.

Overall Pressure: 2.07 MPa (295 psi)

Overall Reactor Composition (mol fraction): C_2H_4 = 0.333, isopentane = .04-01, C_6H_{12} = 0.047, C_6H_{14} = 0.009, H_2 = 0.06, N_2 = 0.511 - 0.451.

Heat of Polymerization = 3721600 J/kg (1600 BTU/lb)

Production Rate = 7131 g/s (56,600 lb/hr)

Cycle Stream Mass Flow Rate = 303655 g/s (2,410,000 lb/hr).

Average Gas Heat Capacity (from example 1) = 1814 J/kg-°C (0.78 BTU/lb-°C)

Average Liquid Heat of Vaporization (from example 1) = 188173 J/kg (80.9 BTU/lb)

ΔT_{max} Across Reaction Zone (i.e., no evaporation) \cong 48.2°C

[0032] Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % Reaction Heat Removed by Vaporization) = 46.4

Isopentane Mole Fraction	0.04	0.05	0.06	0.07	0.08	0.09	0.1
N_2 Mole Fraction	0.511	0.501	0.491	0.481	0.471	0.461	0.451
Inlet Temp. (°C)	50	50	50	50	50	50	50
Dew Point (°C)	67.6	69.2	70.7	72.3	73.8	75.5	76.7
Wt. % Liquid	10.2	11.2	13.1	14.6	16.2	18.1	19.5
ΔT across reaction zone (°C)	41.9	41.2	39.8	38.7	37.4	35.9	34.7
% Reaction Heat Removed by Evaporation	22	24.1	28.2	31.4	34.9	39	42

Example 3: Actual polyethylene production with condensing/evaporation.

[0033] Example 3 shows actual polyethylene production data in condensing mode operation. This example shows that "real-life" data meets the criteria specified by the invention. The measured ΔT fall between the calculated limits. Stable operation was achieved.

Reaction Conditions:

[0034]

Overall Pressure: 2.07 MPa (295 psi)

Overall Reactor Composition (mol %): C_2H_4 = 0.333, isopentane = 0.093, C_6H_{12} = 0.047, C_6H_{14} = 0.009, H_2 = 0.06, N_2 = 0.458.

Heat of Polymerization = 3721600 J/kg (1600 BTU/lb)

Production Rate = 7131 g/s (56,600 lb/hr)

Cycle Stream Mass Flow Rate = 303655 g/s (2,410,000 lb/hr)

ΔT Across Reaction Zone = 36°C

Reactor Inlet Temperature = 51°C

Calculations:**[0035]**

- 5 Dew Point = 75.7°C
 Calculated Liquid Wt. % at Reactor Inlet = 18.8
 Calculated ΔT across reaction zone = 35.3°C
 ΔT_{\max} Across Reaction Zone (i.e., no evaporation) \cong 48.2°C
 10 Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % Reaction Heat Removed by Vaporization) = 46.4

Example 4: Polypropylene Production:

- 15 **[0036]** Example 4 is a simulation of commercial polypropylene production. This example shows how ΔT across the reaction zone can be used to control liquid evaporation. It also shows how the criteria of the invention can be used to discern unstable conditions. It further shows the enhanced sensitivity of the reaction zone ΔT control method over inlet temperature control. The stable control range for inlet temperature is \cong 1°C vs. 9°C for the ΔT control method.

- Overall Pressure: 2.94 MPa gauge (420 psig)
 Overall Reactor Composition (mol %): $C_3H_6 = 0.9$, $H_2 = 0.0025$, $N_2 = 0.0975$.
 20 Calculated Dew Point = 59.7°C
 Heat of Polymerization = 2442.3 kJ/kg (1050 BTU/lb)
 Production Rate = 2520 g/s (20,000 lb/hr)
 Cycle Stream Mass Flow Rate = 248846 g/s (1,975,000 lb/hr)
 Average Gas Heat Capacity \cong 2489 J/kg-°C (1.07 BTU/lb-°C)
 25 Average Liquid Heat of Vaporization \cong 237 kJ/kg (102 BTU/lb).
 ΔT_{\max} Across Reaction Zone (i.e., no evaporation) \cong 9.9°C
 Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % Reaction Heat Removed by Vaporization) = 10.4

30

35

40

45

50

55

Inlet Temp. (°C)	58	58.5	58.8	59	59.5	59.7	60
Wt. % Liquid	15.4	14.3	11.4	9.4	4.4	2.4	0
Enthalpy of Gas (kJ/kg-mol) ((BTU/lb-mol))	(4045) 9409	(4046) 9411	(4061) 9446	(4071) 9469	(4095) 9525	(4104) 9546	(4119) 9581
Enthalpy of (kJ/kg-mol) ((BTU/lb-mol))	(-230) -535	(-217) -505	(-203) -472	(-193) -449	(-169) -393	(-159) -370	(-143) -333
ΔT across reaction zone (°C)	0	0	0	1.08	6.0	7.8	9.9
% Reaction Heat Removed by Evaporation	100 (Unstable)	100 (Unstable)	100 (Unstable)	90.8	42.2	23	0

Example 5: P lypropylene Production:

[0037] Example 5 is a simulation of commercial polypropylene production. This example shows the addition/deletion of liquid propylene feed (i.e., propylene concentration) can be used to control ΔT across the reaction zone.

Overall Pressure: 2.94 MPa gauge (420 psig)
 Overall Reactor Composition (mol %): $C_3H_6 = 0.9-0.91$, $H_2 = 0.0025$, $N_2 = 0.0975-0.0875$.
 Heat of Polymerization = 2442.3 kJ/kg (1050 BTU/lb)
 Production Rate = 2520 g/s (20,000 lb/hr)
 Cycle Stream Mass Flow Rate = 248846 g/s (1,975,000 lb/hr)
 Average Gas Heat Capacity $\cong 2489$ J/kg \cdot $^{\circ}C$ (1.07 BTU/lb \cdot $^{\circ}C$)
 Average Liquid Heat of Vaporization $\cong 237$ kJ/kg (102 BTU/lb)
 ΔT_{max} Across Reaction Zone (i.e., no evaporation) $\cong 9.9^{\circ}C$
 Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % Reaction Heat
 Removed by Vaporization) = 10.4

Propylene Mole Fraction	0.9	0.9025	0.905	0.9075	0.91
N ₂ Mole Fraction	0.0975	0.095	0.0925	0.09	0.0875
Inlet Temp. ($^{\circ}C$)	59.7	59.7	59.7	59.7	59.7
Dew Point ($^{\circ}C$)	59.7	59.9	60.1	60.4	60.6
Wt. % Liquid	2.4	4.6	6.8	9.2	11.7
ΔT across reaction zone ($^{\circ}C$)	7.8	5.8	3.7	1.3	0
% Reaction Heat Removed by Evaporation	23	44.1	65.2	88.3	100 (unstable)

Example 6: Actual polypropylene production with condensing/evaporation.

[0038] Example 6 shows actual polypropylene production data in condensing mode operation. This example shows that the more complex thermodynamic calculations at the reactor inlet conditions (examples 4 and 5) do not agree with observed reactor behavior. Actual run data using the present invention would indicate 90.5% of reaction heat removed by vaporization while the more complex thermodynamic simulation shows only 31.8% of reaction heat removed by vaporization, underestimating the ΔT method by a considerable margin.

[0039] In this case, though both methods use a thermodynamic simulation to predict the extent of condensing, a direct measurement of evaporation in the reaction zone via ΔT would be preferred since it is inherently more stable and does not rely on any calculations to be used by the control method. Assuming that the ΔT method more accurately predicts condensing (a good assumption for PP production due to its higher sensitivity as shown in example 5), this example also shows that an unstable operating condition could be avoided using the present invention as compared to conventional condensing mode calculations.

Reaction Conditions:

[0040]

Overall Pressure: 3.64 MPa gauge (520 psig)
 Overall Reactor Composition (mol %): $C_3H_6 = 0.79$, $C_3H_8 = 0.045$, $H_2 = 0.025$, $N_2 = 0.14$.

Heat of Polymerization = 2442.3 kJ/kg (1050 BTU/lb)
 Production Rate = 4586 g/s (36,400 lb/hr)
 Cycle Stream Mass Flow Rate = 33,389 g/s (2,650,000 lb/hr)
 ΔT Across Reaction Zone = 1.5°C (90.5% of reaction heat removed by vaporization)
 Reactor Inlet Temperature = 63.5°C

Calculations:**[0041]**

Dew Point = 63.7°C
 Calculated Liquid Wt. % at Reactor Inlet = 4.5
 Calculated ΔT across reaction zone = 9.6°C (31.8% of reaction heat removed by vaporization) using reactor inlet composition, temperature, pressure.
 ΔT_{\max} Across Reaction Zone (i.e., no evaporation) \cong 13.5°C
 Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % reaction heat removed by Vaporization) = 14.1

Example 7: Actual polypropylene production with condensing/evaporation.

[0042] Example 7 shows actual polypropylene production data in condensing mode operation. This example again shows that conventional condensing calculations (examples 4 and 5) do not agree with observed reactor behavior. Actual run data indicate 68% of reaction heat removed by vaporization while thermodynamic simulation estimates show only 23.1% of reaction heat removed by vaporization. As in Example 6, a direct measurement of evaporation in the reaction zone via ΔT gives better reaction control.

Reaction Conditions:**[0043]**

Overall Pressure: 3.05 MPa gauge (435.5 psig)
 Overall Reactor Composition (mol %): C_3H_6 = 0.843, C_3H_8 = 0.0518, H_2 = 0.00201, N_2 = 0.104.
 Heat of Polymerization = 2442.3 kJ/kg (1050 BTU/lb)
 Production Rate = 5481 g/s (43,500 lb/hr)
 Cycle Stream Mass Flow Rate = 255776 g/s (2,030,000 lb/hr)
 ΔT Across Reaction Zone = 7.8°C (68 % of reaction heat removed by vaporization)
 Reactor Inlet Temperature = 61.1°C

Calculations:**[0044]**

Dew Point = 61.4°C
 Calculated Liquid Wt. % at Reactor Inlet = 5.1
 Calculated ΔT across reaction zone = 17.0°C (23.1% of reaction heat removed by vaporization) using reactor inlet composition, temperature, pressure.
 ΔT_{\max} Across Reaction Zone (i.e., no evaporation) \cong 21.0°C
 Maximum Wt. % Liquid at Reactor Inlet (i.e., 100 % reaction heat removed by Vaporization) = 22.1

Claims

1. A process for controlling a continuous gas phase exothermic process in a reactor having

- (1) a reactor inlet;
- (2) a reactor bed;
- (3) a reactor outlet; and
- (4) a recycle line with (a) a compressor and (b) a heat exchanger;

with a pre-selected temperature for the reactor bed or outlet (2 or 3) and with a temperature differential (ΔT) between the temperature of the reactor inlet (1) and the pre-selected temperature of the reactor bed or outlet (2 or 3), comprising:

(A) controlling the heat transfer provided by the heat exchanger (4(b)) to maintain the pre-selected reactor bed (2) or outlet (3) temperature, while simultaneously

(B) controlling the feed rate to the reactor of a condensable fluid to maintain the temperature differential (ΔT) constant.

2. A process according to claim 1 wherein ΔT is controlled via the following relation:

$$\Delta T = \frac{(P.R.)(\Delta H_r) - (\dot{m})(x_l)(\Delta H_v)}{(\dot{m})(1-x_l)(C_p)_{\text{cyclegas}}}$$

where (P.R.) = production rate, (ΔH_r) = heat of reaction, (\dot{m}) = cycle gas stream mass flow rate; (x_l) = mass fraction of liquid in the cycle gas stream at reactor inlet, (ΔH_v) = heat of vaporization, and (C_p)_{cyclegas} = heat capacity of the cycle gas.

3. A process according to claim 2 wherein the process control follows the following limitations:

$$(1) \quad (P.R.)(\Delta H_r) \geq (\dot{m})(x_l)(\Delta H_v);$$

$$(2) \quad \Delta T \leq \frac{(P.R.)(\Delta H_r)}{(\dot{m})(C_p)_{\text{cyclegas}}};$$

and

$$(3) \quad \left. \frac{\partial(P.R.)}{\partial(\dot{m}(x_l))} \right|_{\substack{\text{Catalyst Feed,} \\ \text{Other Independent} \\ \text{Variables Constant}}} \geq 0.$$

4. A process according to any one of the preceding claims wherein the exothermic process is a polymerization reaction to manufacture polypropylene homopolymers or copolymers, ethylene-propylene rubber, ethylene-propylene-diene rubber or polyethylene homopolymers or copolymers.

5. A process according to any one of the preceding claims wherein the condensable fluid is a reactant.

6. A process according to any one of the preceding claims wherein the reactant feed introduced in the reactor inlet comprises a condensable fluid and a reactant.

7. A process according to any one of the preceding claims wherein the condensable fluid is selected from the group consisting of propane, n-butane, isobutane, n-pentane, isopentane, neopentane, n-hexane, isohexane, n-heptane, n-octane, other saturated C₇ and C₈ hydrocarbons, propylene, 1-butene, isobutene, hexene, hexadiene, isoprene, styrene, octadiene, ethylidene norbornene, butadiene and mixtures thereof.

8. A process according to any one of the preceding claims, wherein there are thermocouples measuring the reactor inlet, bed, and outlet temperatures and the selected temperature differential (ΔT) is determined from these thermocouples.

9. A process according to claim 8 wherein the measured temperature differential (ΔT) is linked operationally to the

amount of condensable fluid entering the reactor via a reactor feed line.

10. A process according to claim 8 wherein the measured temperature differential ΔT is operationally linked to the amount of heat transfer provided by the heat exchanger and to the mass flow through the recycle line.

Patentansprüche

1. Verfahren zur Kontrolle eines kontinuierlichen exothermen Gasphasen-Prozesses in einem Reaktor mit

- (1) einem Reaktoreinlass;
- (2) einem Reaktorbett;
- (3) einem Reaktorauslass, und
- (4) einer Recycle-Leitung mit (a) einem Kompressor und (b) einem Wärmeaustauscher;

mit einer ausgewählten Temperatur für das Reaktorbett oder den Reaktorauslass (2 oder 3) und mit einem Temperaturunterschied (ΔT) zwischen der Temperatur des Reaktoreinlasses (1) und der ausgewählten Temperatur des Reaktorbettes oder des Reaktorauslasses (2 oder 3), umfassend

(A) Kontrollieren der durch den Wärmeaustauscher (4(b)) bereitgestellten Wärmeübertragung, um die ausgewählte Reaktorbett- (2) oder Reaktorauslass- (3) Temperatur zu halten, während gleichzeitig

(B) die Zufuhr eines kondensierbaren Fluids zu dem Reaktor kontrolliert wird, um den Temperaturunterschied (ΔT) konstant zu halten.

2. Verfahren nach Anspruch 1, wobei ΔT durch die folgende Gleichung kontrolliert wird:

$$\Delta T = \frac{(P.R.)(\Delta H_r) - (\dot{m})(x_l)(\Delta H_v)}{(\dot{m})(1-x_l)(C_p)_{\text{Kreislaufigas}}}$$

wobei (P.R.)=Produktionsrate, (ΔH_r) =Reaktionswärme, (\dot{m}) =Massenflussrate des Kreislaufigasstroms; (x_l) =Flüssigkeits-Massenfraktion in dem Kreislaufigasstrom am Reaktoreinlass, (ΔH_v) =Verdampfungswärme und $(C_p)_{\text{Kreislaufigas}}$ =Wärmekapazität des Kreislaufigases.

3. Verfahren nach Anspruch 2, wobei die Prozesskontrolle den folgenden Grenzen folgt:

$$(1) \quad (P.R.)(\Delta H_r) \geq (\dot{m})(x_l)(\Delta H_v)$$

$$(2) \quad \Delta T \leq \frac{(P.R.)(\Delta H_r)}{(\dot{m})(C_p)_{\text{Kreislaufigas}}};$$

und

$$(3) \quad \left. \frac{\partial(P.R.)}{\partial[\dot{m}(x_l)]} \right|_{\substack{\text{Katalysator-Zufuhr} \\ \text{andere unabhängige} \\ \text{Variablen konstant}}} \geq 0.$$

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei der exotherme Prozess eine Polymerisationsreaktion zur Herstellung von Polypropylen-Homopolymeren oder -Copolymeren, Ethylen-Propylen-Gummi, Ethylen-Propylen-Dien-Kautschuk oder Polyethylen-Homopolymeren oder -Copolymeren ist.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei das kondensierbare Fluid ein Reaktant ist.
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die in den Reaktoreinlass eingeführte Reaktanten-Zufuhr ein kondensierbares Fluid und einen Reaktanten umfasst.
7. Verfahren nach einem der vorhergehenden Ansprüche, wobei das kondensierbare Fluid ausgewählt wird aus der Gruppe bestehend aus Propan, n-Butan, Isobutan, n-Pentan, Isopentan, Neopentan, n-Hexan, Isohexan, n-Heptan, n-Octan, anderen gesättigten C₇- und C₈-Kohlenwasserstoffen, Propylen, 1-Buten, Isobuten, Hexen, Hexadien, Isopren, Styrol, Octadien, Ethyldennorbornen, Butadien und Mischungen davon.
8. Verfahren nach einem der vorhergehenden Ansprüche, wobei Thermoelemente vorhanden sind, die die Temperaturen des Reaktoreinlasses, Reaktorbetts und Reaktorauslasses messen, und der ausgewählte Temperaturunterschied (ΔT) über diese Thermoelemente bestimmt wird.
9. Verfahren nach Anspruch 8, wobei der gemessene Temperaturunterschied (ΔT) mit der Menge kondensierbaren Fluids, das via eine Reaktor-Zufuhrleitung in den Reaktor eintritt, betriebsmäßig gekoppelt wird.
10. Verfahren nach Anspruch 8, wobei der gemessene Temperaturunterschied ΔT mit dem von dem Wärmeaustauscher bereitgestellten Ausmaß an Wärmeübertragung und mit dem Massenfluss durch die Recycle-Leitung betriebsmäßig gekoppelt wird.

Revendications

1. Procédé permettant de contrôler un processus exothermique continu en phase gazeuse, dans un réacteur comprenant

- 1) une entrée de réacteur,
- 2) un lit de réacteur,
- 3) une sortie de réacteur, et
- 4) une conduite de recyclage comportant

- a) un compresseur et
- b) un échangeur thermique,

étant données une valeur présélectionnée de la température du lit (2) de réacteur ou à la sortie (3) du réacteur et une certaine valeur de la différence de température ΔT entre la température à l'entrée (1) du réacteur et la température présélectionnée du lit (2) de réacteur ou à la sortie (3) du réacteur, ledit procédé comportant

- A) le fait de régler le transfert de chaleur opéré par l'échangeur thermique (4b), de manière à maintenir à sa valeur présélectionnée la température du lit (2) de réacteur ou à la sortie (3) du réacteur, et simultanément,
- B) le fait de régler le débit d'alimentation du réacteur en fluide condensable de manière à maintenir constante la différence de température ΔT .

2. Procédé conforme à la revendication 1, dans lequel ΔT obéit à la relation suivante :

$$\Delta T = \frac{(VP) \cdot (\Delta H_r) - (m')(x_i)(\Delta H_v)}{(m')(1-x_i)(C_{p(g)})}$$

dans laquelle

- VP représente la vitesse de production,
 ΔH_r représente la chaleur de réaction,
 m' représente le débit massique du courant de gaz de recyclage,
 x_i représente la fraction massique de liquide dans le courant de gaz de recyclage à l'entrée du réacteur,
 ΔH_v représente la chaleur de vaporisation,

et $C_{p(gr)}$ représente la capacité calorifique du gaz de recyclage.

3. Procédé conforme à la revendication 2, dans lequel le contrôle de processus est soumis aux restrictions suivantes :

$$1) \quad (VP) \cdot (\Delta H_r) \geq (\dot{m})(X_i)(\Delta H_v)$$

$$2) \quad \Delta T \leq (VP) \cdot (\Delta H_r) / (\dot{m})(C_{p(gr)})$$

$$3) \quad \partial(VP) / \partial(\dot{m})(X_i) \geq 0 \text{ (l'alimentation en catalyseur et les autres variables indépendantes étant maintenues constantes).}$$

4. Procédé conforme à l'une des revendications précédentes, dans lequel le processus exothermique est une réaction de polymérisation produisant des homopolymères ou copolymères du propylène, un caoutchouc d'éthylène/propylène, un caoutchouc d'éthylène/propylène/diène, ou des homopolymères ou copolymères de l'éthylène.

5. Procédé conforme à l'une des revendications précédentes, dans lequel le fluide condensable est un réactif.

6. Procédé conforme à l'une des revendications précédentes, dans lequel le courant d'alimentation en réactif, amené à l'entrée du réacteur, contient un fluide condensable et un réactif.

7. Procédé conforme à l'une des revendications précédentes, dans lequel le fluide condensable est choisi dans l'ensemble que constituent les propane, n-butane, isobutane, n-pentane, isopentane, néopentane, n-hexane, isohexane, n-heptane et n-octane, les autres hydrocarbures saturés en C_7 ou en C_8 , et les propylène, 1-butène, isobutène, hexène, hexadiène, isoprène, styrène, octadiène, éthylidène-norbornène et butadiène, ainsi que leurs mélanges.

8. Procédé conforme à l'une des revendications précédentes, dans lequel des thermocouples permettent de mesurer la température à l'entrée, dans le lit et à la sortie du réacteur, et la différence de température ΔT choisie est déterminée à l'aide de ces thermocouples.

9. Procédé conforme à la revendication 8, dans lequel la différence de température ΔT mesurée est opérationnellement reliée à la quantité de fluide condensable qui pénètre dans le réacteur par une conduite d'alimentation du réacteur.

10. Procédé conforme à la revendication 8, dans lequel la différence de température ΔT mesurée est opérationnellement reliée à la quantité de chaleur transférée par l'échangeur de chaleur et au débit massique dans la conduite de recyclage.

Figure 1

